Photochemical treatment of pharmaceuticals

Andersen, Henrik Rasmus; Hansen, Kamilla Marie Speht; Kosjek, T.; Heath, E.; Kaas, P.; Ledin, Anna

Publication date:
2008

Photochemical treatment of pharmaceuticals

H.R. Andersen[*], K.M.S. Hansen*, T. Kosjek[**], E. Heath[2**], P. Kaas[***], A. Ledin[****]

*Inst. of Environment & Resources, Technical University of Denmark, Denmark,
** Jožef Stefan Institute, Slovenia,
[***]Scan Research A/S, Denmark
[****]Dep. of Water and Environmental Studies, Linköping University, Sweden

Keywords: Pharmaceuticals, carbamazepine, clofibric acid, UV, AOP, Electrical Energy per Order.

INTRODUCTION

Few pharmaceuticals are not removed in conventional sewage treatment, among the most important of these in terms of high consumption volume are carbamazepine [Clara, 2005], clofibric acid [Clara et al., 2005; Kosjek et al., 2007] and diclofenac [Kosjek et al., 2007]. It is known that the above mentioned three stable pharmaceuticals can be photo-degraded in surface waters by sunlight [Doll & Frimmel, 2003, Petrovic & Barceló, 2007]. This is likely the most important ultimate fate of non bio-degradable and non-sorbing pharmaceuticals. The UV-absorption spectra of carbamazepine and clofibric acid [Doll & Frimmel, 2003] shows that carbamazepine absorbs from 320 nm with a local maximum at 280 nm. Clofibric acid absorbs weakly between $300-240$ and has a local maximum at 230 nm. Sunlight has very little intensity below 320 nm and even most sunlight below 400 nm is filtered by the atmosphere. UV lamps used e.g. for photo-chemicals reactions and disinfection of water can create a many fold more intensively illumination of water with a higher fractions of light having lower wavelengths thus potentially decreasing half lives of pharmaceuticals to the seconds time scale.

The aim of this study was to investigate the removal efficiency of six pharmaceuticals by photo-degradation and the advanced oxidation process (AOP), UV/H_2O_2. The six pharmaceuticals were the four non-steroidal-anti-inflamatory drugs: ibuprofen, diclofenac, naproxen and ketoprofen, the pharmacological active metabolite of the lipid lowering agent, clofibrin, clofibric acid, and the anticonvulsant and mood stabilizing drug, carbamazepine.

METHOD

Treatment experiments were performed using a UV lamp optimized for photochemical treatment in a flow through set-up. For the AOP experiments 60 mg/L H_2O_2 was added to the water before treatment. Tap water and treated sewage were spiked with 10 µg/L of each of the pharmaceuticals. The treatment effectiveness is evaluated based on the Electrical Energy per Order (EEO) (unit kWh/m^3), which is defined as the electrical energy consumed per unit volume of water treated required for 90 % removal of the investigated compound [Bolton et al., 2001].

RESULTS AND DISCUSSION

It was found that four of the six pharmaceuticals were almost completely removed in tap water both by UV treatment and by the AOP with the lowest treatment dosis of UV applied in the experiment, making it difficult to determine the exact removal efficiency. The exception was ibuprofen and carbamazepine, which exhibited a relationship between UV dose and removal (figure 1). The EEO was determined to 22.7 kWh/m^3 (UV) and 3.7 kWh/m^3 (UV/H_2O_2) for carbamazepine and 8.6 kWh/m^3 (UV) and 3.7 kWh/m^3 (UV/H_2O_2) for

ibuprofen (Table 1). However, all pharmaceuticals can be removed with UV treatment alone and therefore removal in wastewater was only tested by UV-treatment.

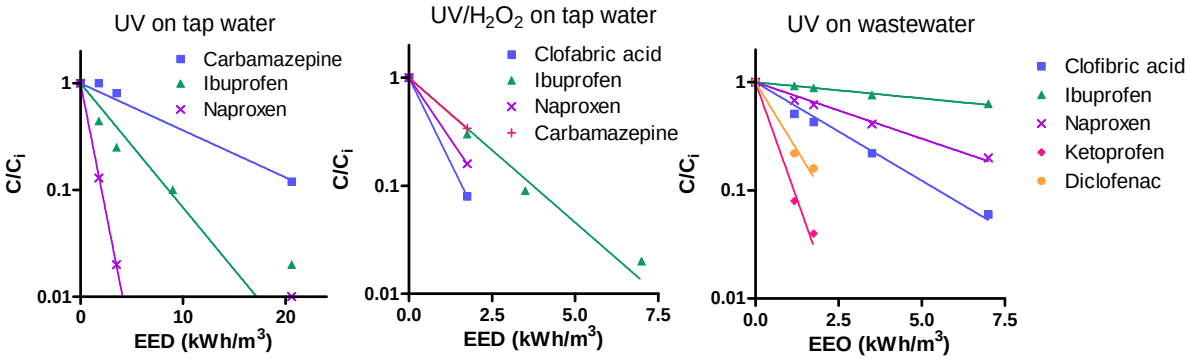

Figure 1: Energy effectiveness of removal of pharmaceuticals.

In the wastewater effluent the removal by UV was almost complete for ketoprofen even at the lowest treatment effect, while the other compounds show dependency of energy/UV dose applied (Table 1, Figure 1).

Table 1: Energy needed for reducing concentrations by one decade.

	Tap water		Wastewater effluent
	UV EEO ± 95% CI	UV/H_2O_2 EEO ± 95% CI	UV EEO ± 95% CI
Clofibric acid	-	1.6[a]	5.5 ± 0.6
Ibuprofen	8.6 ± 4.4	3.7 ± 0.7	33.4 ± 3.4
Naproxen	2.1 ± 0.9	2.2[a]	9.6 ± 1.1
Ketoprofen	-	-	1.2 ± 0.3
Diclofenac	-	-	2.0 ± 0.6
Carbamazepine	22.7 ± 4.1	3.7[a]	-

[a] Regression with only two points.

Ibuprofen is the compound that required the highest UV dose to remove 90 % from wastewater (EEO = 33.4 kWh/m^3) where naproxen and clofibric acid required 9.6 kWh/m^3 and 5.5 kWh/m^3, respectively. Ketoprofen and diclofenac needed considerable less energy than clofibric acid. Ibuprofen and naproxen are biodegradable and will be removed in biologically treated wastewater. Therefore the relevant estimate of the needed treatment is the energy use for removal of clofibric acid which required 5.5 kWh/m^3 for 90 % removal.

References

Bolton, J. R., Bircher, K. G., Tumas, W., and Tolman, C. A. (2001), Figures-of-merit for the technical development and application of advanced oxidation technologies for both electric- and solar-driven systems. Pure and Applied Chemistry, 73(4):627–638.

Clara,M., Strenn,B., Gans,O., Martinez,E., Kreuzinger,N., and Kroiss,H. (2005) Removal of selected pharmaceuticals, fragrances and endocrine disrupting compounds in a membrane bioreactor and conventional wastewater treatment plants. *Water Research* **39** (19), 4797-4807.

Doll,T.E. and Frimmel,F.H. (2003) Fate of pharmaceuticals--photodegradation by simulated solar UV-light. *Chemosphere* **52** (10), 1757-1769.

Kosjek T., Heath E., Kompare B., (2007) Removal of pharmaceuticals residues in a pilot wastewater treatment plant. Analytical and Bioanalytical Chemistry. 387/4: 1379-1387

Petrovic,M. and Barceló,D. (2007) LC-MS for identifying photodegradation products of pharmaceuticals in the environment. *Trends in Analytical Chemistry* **26** (6), 486-493.